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Comparison between the Effect of Permanganate/Sodium Chloride and That of Permanganate/Water upon Wool

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The modification of practical properties of wool by the potassium permanganate/sodium chloride treatment can be attributed to the fact that the reaction is localized upon the surface of fibers, while in the case of potassium permanganate/water treatment reaction proceeds deep into the interior of fibers. Several examples are given in evidence. (1) The anti-scale coefficient of friction decreases markedly by the permanganate/sodium chloride treatment, and the difference from the with-scale coefficient becomes smaller. This means that the directional effect diminishes. (2) The electron photomicrographs of the surface of the permanganate/sodium chloride treated fibers show that the edges of scales are considerably rounded. (3) Manganese dioxide which deposits after the treatment by potassium permanganate in the presence of sodium chloride concentrates upon the exterior of fibers, while it diffuses into the depth of fibers when treated in the absence of the salt. (4) Estimation of surface damage by staining the fibers with Methylene Blue also supports the conclusion that the outside of fibers is predominantly affected by the permanganate/sodium chloride treatment.

1. COEFFICIENT OF FRICTION OF WOOL

While the permanganate/sodium chloride system has a pronounced shrinkproofing effect upon wool, the permanganate/water system is less effective. According to McPhee^{1,2)} and Bradbury³⁾, this cannot be simply explained by the assumption that, in the case of permanganate/sodium chloride treatment, the oxidative reaction is confined only to the surface of fibers by the reduction of swelling caused by sodium chloride. The reason for the opinion consists in the fact that the "directional frictional effect" of permanganate/salt treated fibers does not differ appreciably from that of permanganate/water treated fibers.

As mentioned above it has been attempted in this study to measure the frictional coefficient between the fiber to be tested and the top of fibers of the same species. Further, in order to correlate the results of measurements with the shrinkage of yarns and fabrics, it was important to measure the coefficient of friction in wet state. For this purpose, the fiber to be tested and the top with which the fiber comes in contact were wetted by the buffered solution of pH 3 and 9, and 0.05% soap solution.

In Table 1 the anti-scale coefficients of friction (μ_1) and the with-scale coefficients of friction (μ_2) of untreated fibers, permanganate/sodium chloride treated fibers and permanganate/water treated fibers are given. It can be seen that the with-scale coefficient μ_2 is not changed appreciably by the permanganate/sodium

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Table 1. Frictional properties of fibers, treated with permanganate/sodium chloride and permanganate/water compared to those of untreated fibers.

Buffered at pH 3			
	μ_1	μ_2	$\mu_1 - \mu_2$
Untreated	0.67 ± 0.06	0.24 ± 0.03	0.43 ± 0.02
5% KMnO_4 in NaCl soln.	0.39 ± 0.04	0.28 ± 0.02	0.11 ± 0.01
5% KMnO_4 in water	0.63 ± 0.11	0.26 ± 0.03	0.37 ± 0.02
Buffered at pH 9			
	μ_1	μ_2	$\mu_1 - \mu_2$
Untreated	0.57 ± 0.12	0.20 ± 0.02	0.37 ± 0.03
5% KMnO_4 in NaCl soln.	0.36 ± 0.05	0.24 ± 0.02	0.12 ± 0.03
5% KMnO_4 in water	0.53 ± 0.11	0.23 ± 0.03	0.30 ± 0.02
0.05% soap solution			
	μ_1	μ_2	$\mu_1 - \mu_2$
Untreated	0.62 ± 0.06	0.20 ± 0.02	0.42 ± 0.02
5% KMnO_4 in NaCl soln.	0.38 ± 0.07	0.23 ± 0.02	0.15 ± 0.01
5% KMnO_4 in water	0.42 ± 0.02	0.23 ± 0.01	0.19 ± 0.02

chloride treatment as it is by the permanganate/water treatment, but the anti-scale coefficient μ_1 is strikingly decreased by the permanganate/sodium chloride treatment. In this case, therefore, the directional property $\mu_1 - \mu_2$ is markedly decreased. On the other hand, the permanganate/water treatment results in a smaller effect upon the frictional behavior of wool. In agreement with this, the yarns and fabrics are shrinkproofed only to a smaller extent by the permanganate/water treatment, as has been shown in the previous paper⁴⁾. If it is reckoned that the felting and shrinkage of wool owe greatly to the surface character of wool, these results are very significant as showing the close correlation between them. The fact that the change in frictional coefficient by the treatment has not been found by McPhee and other authors might be due to the method they employed, which would not be adequate to prove the change in surface character of fiber as happens during the permanganate treatments.

2. ELECTRON MICROSCOPIC OBSERVATIONS

The changes in various properties of wool resulting from permanganate/sodium chloride treatment, such as decrease in shrinkage, anti-scale coefficient of friction, pilling, and increase in dye-accessibility and so forth, have suggested that the surface character of wool would have been modified considerably by the treatment. This can be clearly demonstrated by the observation with an electron microscope. Fig. 1 shows some examples of electron photomicrographs of the replicas of the surface of untreated fibers and treated fibers. It can be seen that the surface of permanganate/sodium chloride treated fibers is considerably damaged and the edges of the scales are remarkably rounded. It can be inferred from the figure that the directional effect of friction of the treated fibers would be smaller than that of the untreated fibers, as was actually shown in the previous section.

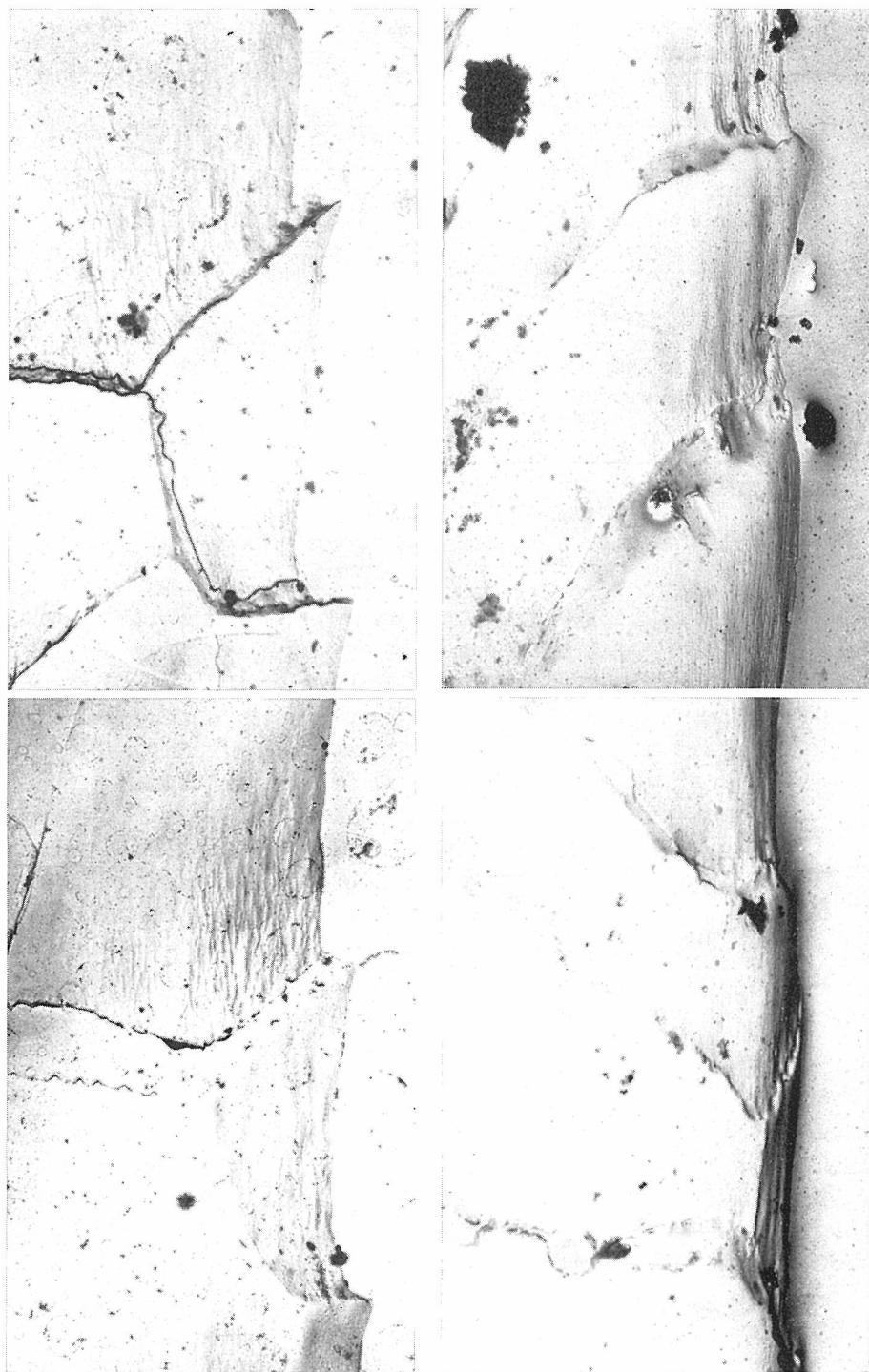


Fig. 1. Electron photomicrographs of the replicas of the untreated fibers (left) and those of the permanganate/sodium chloride treated fibers (right).

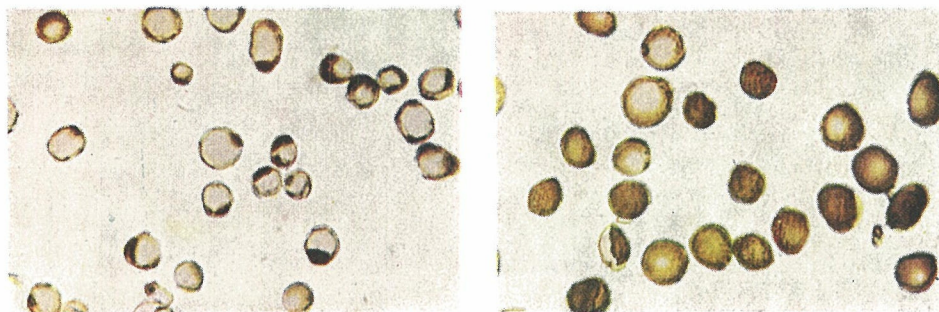


Fig. 2. Deposition of manganese dioxide within fibers. The left photomicrograph shows the cross-sections of the fibers treated with permanganate/sodium chloride, and the right one the cross-sections of fibers treated with permanganate/water.

3. DEPOSITION OF MANGANESE DIOXIDE WITHIN THE FIBER

If the process of reduction is eliminated from the permanganate treatments, the deposited manganese dioxide is left within the fiber, which can be detected by examining the cross-sections. Fig. 2 shows the photomicrographs of cross-sections of fibers treated with permanganate/sodium chloride and those of fibers treated with permanganate/water. In the case of permanganate/sodium chloride treatment, manganese dioxide deposits only at the outside of fibers, but in the case of permanganate/water treatment, manganese dioxide is found penetrated deeper into the fibers, and in many cases the whole cross-section is uniformly stained by manganese dioxide. This suggests that, in the presence of sodium chloride, the reaction is limited to the outside of fibers, while in the absence of

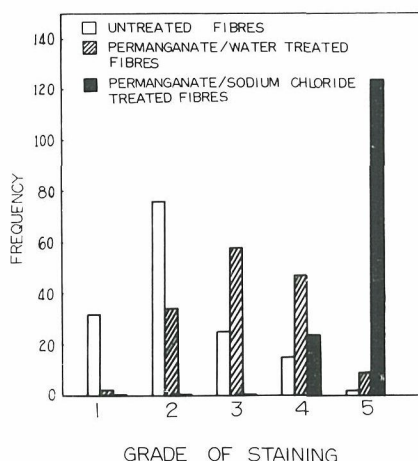


Fig. 3. Sorting of stained fibers according to the degree of staining. The ordinate shows the frequency and the abscissa the grade of staining.

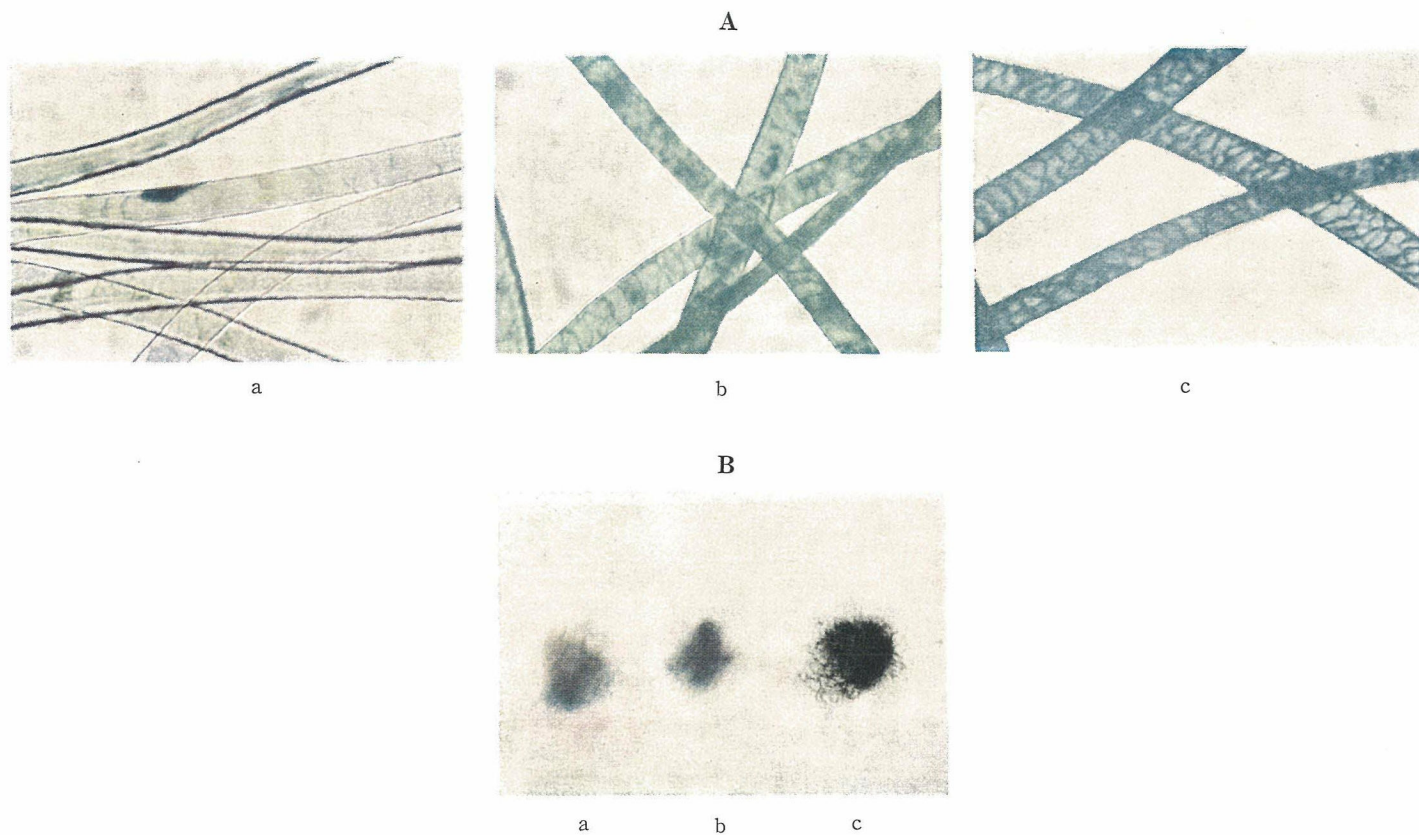


Fig. 4. Photographs of the stained fibers. A-series shows the photomicrographs and B-series the direct photographs.
 (a) Untreated fibers, (b) Permanganate/water treated fibers, and (c) Permanganate/sodium chloride treated fibers.

sodium chloride, the reaction proceeds into the depth of fibers. Since the amount of reacted permanganate is the same in both the cases, the surface of fibers should be more strongly affected by the permanganate/sodium chloride than by permanganate/water. This is also compatible with the results of the previous sections.

4. ESTIMATION OF SURFACE DAMAGE BY STAINING

The method presented by Whewell and Woods⁵⁾ was used, who estimated the degree of the surface damage of wool fibers by staining them with Methylene Blue under the condition which hardly causes the staining of the sound fibers.

The outline of the method is as follows: 0.1g. of wool is immersed in 100ml. of 0.4g./l. Methylene Blue solution, kept at 20°C for 15 minutes, and is washed with water. The fibers are sorted into five grades, that is—1, 2, 3, 4, and 5 according to the degree of staining standardized arbitrarily, and a frequency diagram is prepared. Grade 1 means perfectly unstainable, while Grade 5 means uniformly stainable of scales by Methylene Blue.

The untreated fibers, the permanganate/water treated fibers and the permanganate/sodium chloride treated fibers were respectively subjected to the staining tests, and a frequency diagram was made each with 160 fibers. Fig. 3 shows the frequency diagram thus obtained.

Most of the permanganate/sodium chloride treated fibers fall within Grade 5 and only partially within Grade 4. The scale damage of the permanganate/water treated fibers is smaller than that of the permanganate/sodium chloride treated fibers, since they scatter over all the grades from 1 to 5 and have a peak at Grade 3. The peak of the untreated fibers is seen at Grade 2.

Fig. 4 represents the photographs of stained fibers and their photomicrographs.

The results of these staining tests also give an evidence for the possibility that the reaction takes place concentrated upon the surface of fibers when they are treated with permanganate in the ample presence of sodium chloride.

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